

Additional β Zeolites in $\text{SiO}_2\text{-Al}_2\text{O}_3$ Supported Pt and Pd Catalysts for Hydrocracking of Paraffin Wax

Jian Jiang¹, Chao Yang¹, Jibing Sun¹, Tao Li^{1,2}, Fahai Cao^{1,2,*}

¹School of chemical engineering, East China University of Science and Technology, Shanghai 200237, China

² Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

*graycoffee@163.com; ²y123438@126.com; ³apollosun1987426@163.com; ⁴tli@ecust.edu.cn; ⁵fhcao@ecust.edu.cn

Abstract

Different Pt/SAB and Pd/SAB (40 wt% SiO_2 in silica-alumina carriers with 20 wt% β zeolites) catalysts were prepared by impregnation method and compared with NiW/SAB catalyst. The results showed that Pt/SAB catalyst had larger surface area and pore volume compared to NiW/SAB and Pd/SAB catalysts. Pt and Pd loading, the reaction parameters of reaction such as temperature and WHSV were investigated. The hydrocracking reaction results showed that 0.8 wt% Pt loading catalyst had optimized conversion ratio and selectivity with 300°C and WHSV=2 h⁻¹. Pd/SAB catalyst had higher gas selectivity but lower naphtha and middle distillates yield due to the strongest acidic sites. Pt/SAB catalyst had more stable catalytic activity during hydrocracking reaction. TEM and ICP results indicated that Pt was highly dispersed in small clusters and stable after 200 h reaction, while Pd and NiW/SAB catalysts had deactivated issue.

Keywords

Hydrocracking; Pd/SAB Catalyst; Pt/SAB Catalyst; Deactivation

Introduction

Cleaner fuels can be obtained by natural gas, coal and biomass conversion to liquid fuels via F-T technology and alleviate the energy shortage caused by crude oil fluctuation. The hydrocracking reaction is applied to produce middle distillates which can cut long chain hydrocarbon. Shell, Exxon, Sasol and other major international petrochemical companies have invested in this field. The hydrocracking catalyst is characterized by the presence of two types of active sites. Acidic sites act as isomerization and cracking function while metal sites have hydrogenation and dehydrogenation function. The noble metal (Pt, Pd) and transition metal (W, Ni, Mo, Co) are commonly used. The noble metal (especially Pt) shows better performances in terms of selectivity and conversion

rate. It also has no sulfur and is more environmental friendly in final products.

Cracking reaction is the key point to control the yield of middle distillates in acidic sites. The acidic sites and materials of carriers have great influence on hydrocracking. It is reported that more weak and middle acidic sites can increase the selectivity of middle distillates. It is well known that amorphous silica-alumina has strong medium acidic site which leads to high yield of middle distillates. On the other hand, zeolite has higher activity of catalyst but lower selectivity of middle distillate. Joong won Lee et al. reported that carriers with 40% (wt %) SiO_2 content in amorphous silica-alumina had the best conversion rate and selectivity Sakoda H et al found that addition of small amount of USY zeolite to amorphous silica-alumina could improve the activity of hydrocracking with slight loss of middle distillates selectivity.

Our previous study described the series of NiW supported catalysts with different supports, $\text{SiO}_2\text{-Al}_2\text{O}_3$ (SA-x), $\text{SiO}_2\text{-Al}_2\text{O}_3$ with H- β zeolites (β -SA-y), were made by the urea-matrix combustion method. The results indicated that the SA-0.4 sample had the highest yield of middle distillate and a promising conversion rate more than 90%. Further, it was found that β -SA-0.2 sample had a comparable yield of middle distillate with SA-0.4 samples (about 84%), while the reaction temperature was 60°C lower. It is essential to conduct the catalytic properties of noble catalyst and compare to NiW metal catalyst.

In this paper, series catalysts of SAB supports with different Pt and Pd loading have been prepared based on β -SA-0.2 sample. The reaction parameters such as temperature, metal loading and WHSV were investigated. The deactivated properties were

conducted among NiW/SAB, Pd/SAB and Pt/SAB catalyst in order to check the industrization possibility. The fixed bed single stainless reactor was employed to study the catalytic activity of hydrocracking reaction.

Experimental

A specific amount of aluminum nitrate (Sinopharm) and sodium silicate (Sinopharm) were dissolved in water and the pH was adjusted to 6 by adding ammonia. The amorphous aluminum nitrate precipitates were obtained, then β zeolites and sodium silicate solution was added into the suspension. Finally, the mixture was stirred for 2 hours and aged at room temperature for 6 h. The supports were filtered, washed with deionized hot water, dried at 120°C for 12 h and finally calcined at 550°C in Muffle furnace for 5 h. The final supports were obtained and it was marked as SAB support. ($\text{SiO}_2/\text{Al}_2\text{O}_3=40$ wt% and β zeolite =20 wt%)

Chloroplatinic acid or Palladium Chloride was dissolved in 25 ml flask. The solution was diluted to the required volume and SAB carriers were added into solution. The mixture was merged at 50°C for 5 h, followed by drying at 120°C for 12 h. Finally, it was calcined at 550°C in Muffle furnace for 5 h. The Pt/SAB or Pd/SAB catalyst was obtained. In accordance with the different ratio of metal loading, Metal-x/SAB means different Pt and Pd loading catalysts (where $x=0.01, 0.008, 0.005, 0.003$ wt).

The surface area and pore structure of the catalysts were determined via physical adsorption measurements (Micro Meritics, ASAP-2020). The metal dispersion of catalyst was conducted by TEM (JEM, TEOL2010) and TPD-NH₃ method was employed to study the acid strength and acid amount of the catalyst. Generally speaking, the temperature of the desorption peaks of less than 200°C, 200-350°C and more than 350°C correspond to the weak, medium and strong acidic sites. The metal stability was conducted by ICP(IRIS 1000, Thermo Elemental).

The semi-refined 56 # wax was taken as model feedstock whose molecular weight was about 300-500 and the carbon number distribution was 19-36. A lab-scale fixed-bed reactor with higher pressure was used in this study, which had a tube of 25 mm internal diameter and 350 mm in length. Each time, 4.3 g catalyst with 50 to 60 meshes was loaded into reactor. The wax and H₂ were introduced into the single-bed reactor with the ratio of H₂/Wax=0.12 wt/wt. The tail gas was collected and analyzed via online GC (GC-900 A). Liquid products were collected and fractionated

into C₅-C₉, C₁₀-C₁₈ and C₁₉+ which were analyzed by GC (FUL9790). Conversion, selectivity were calculated as the same as our previous study.

Results and Discussion

Characterization of the Catalysts

The surface properties of catalysts, such as surface area and average pore diameters, are shown in Table 1. Pt-0.008/SAB and Pd-0.008/SAB catalysts were selected as typical sample for testing. It was clear that the NiW/SAB catalyst has a minimum surface area and pore volume. The surface area and pore volume of the NiW/SiO₂-Al₂O₃ catalyst increased slightly. Whereas the surface area of Pd/SAB and Pt/SAB catalysts increased moderately and pore volume was not changed significantly. The Pt-0.008/SAB catalyst had the biggest surface area and widest pore volume among these three catalysts and it could help the hydrocracking reactions. The average pore diameters of these catalysts were almost the same.

TABLE 1 SURFACE PROPERTIES OF CATALYSTS

Catalysts	S _{BET} (m ² /g)	PV (m ³ /g)	APD (nm)
NiW/ SiO ₂ -Al ₂ O ₃	208	0.503	9.7
NiW/SAB	188	0.467	9.9
Pt-0.008/SAB	240	0.588	9.8
Pd-0.008/SAB	223	0.547	9.9

Notes: S_{BET}; surface area; PV; pore volume; APD; average pore diameter

The weak and moderate acidity of catalyst has great influence on hydrocracking of F-T synthetic wax, therefore the catalysts with different Pt loading and 0.8% Pd loading are conducted by NH₃-TPD and the results are shown in Fig 1.

It can be seen from Fig 1 that the intensities of weak and moderate acidity of different Pt-loading catalysts are significantly different. Pt-0.008/SAB and Pt-0.005/SAB catalysts have the most intensive NH₃ desorption peak around 200-300°C, which corresponds to the dominant weak and moderate acidity, whereas Pt-0.01/SAB catalyst has the peak above 500°C, which relates to the strongest acidity. The results showed that less Pt-loading catalysts could generate higher middle distillate selectivity and higher Pt-loading catalysts may increase the conversion ratio. Pd-0.008/SAB catalyst has strongest acidity, which may link to higher activity and gas selectivity.

As shown in Fig 1, the Pd-0.005/SAB catalyst has minimal weaker and medium acidity. The weaker and medium acidity of Pd-0.001/SAB catalyst increased moderately, whereas the Pt-0.008/SAB catalyst has the

strongest medium acidity. In general, Pd/SAB catalysts have more strong acidity in comparison with Pt/SAB catalysts which could generate more gas and less middle distillates selection.

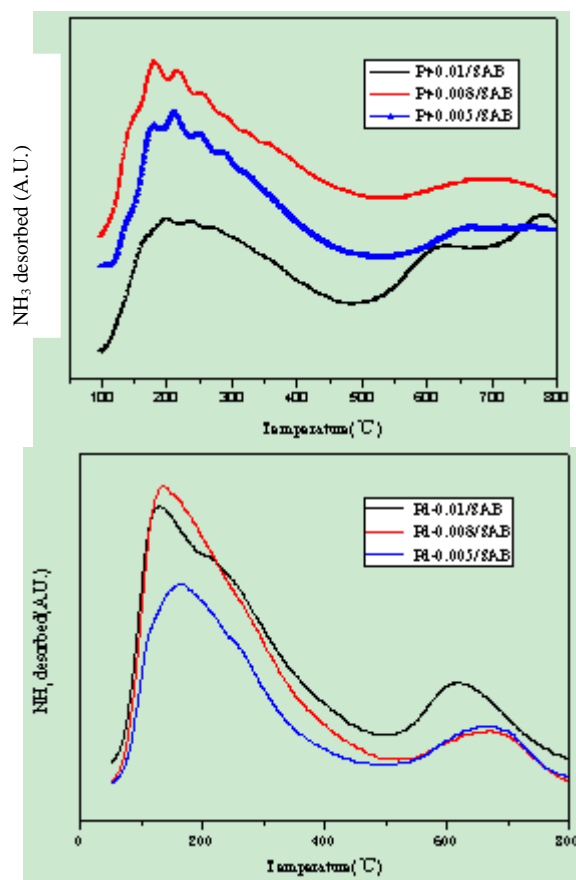


FIG. 1 NH₃-TPD CURVE OF Pt/SAB CATALYST

Catalytic Activity of Pt/SAB Catalyst with Different Pt Loading

With the condition of $T=320^{\circ}\text{C}$, $P=3.5\text{ MPa}$, and $\text{H}_2/\text{wax}=0.12\text{ wt/wt}$, the influence of different Pt loading from 0.3% to 1% (wt%), was investigated. The WHSV was changed from 1 h^{-1} to 2 h^{-1} and the results were shown in Table 2.

With Pt loading increasing, the conversion ratio is significantly increased and the selectivity of gaseous hydrocarbons is risen gradually. The trend is observed that higher conversion ratio and selectivity of naphtha and middle distillates are obtained with higher WHSV. Thereof, Naphtha and MD yield of Pt-0.008 catalyst is 82.31% and the conversion ratio is 98.22% with WHSV = 2 h^{-1} . When Pt loading is increased from 0.008 to 0.01, the conversion ratio is improved while naphtha and MD yield is decreased slightly with different WHSV conditions. Furthermore, less Pt loading with 0.005 and 0.003 have lower conversion ratio and liquid selectivity. It has been indicated that different Pt

loading changes the weak, middle and strong acid sites on the catalyst.

TABLE 2 EFFECT OF DIFFERENT PT LOADING CONTENT ON PT/SAB CATALYST ACTIVITY

Pt-Loading (wt)	T ($^{\circ}\text{C}$)	WH SV (h^{-1})	Selectivity (%)				
			Con version (%)	Gas	Na ph .	M D	Naphtha and MD yield (%)
Pt-0.01	320	1	92.2 2	26.2 1	68. 98	4.8 2	68.06
	320	2	99.4 2	18.0 6	67. 58	14. 36	81.46
Pt-0.008	320	1	91.1 1	15.6 8	67. 78	16. 57	76.85
	320	2	98.2 2	16.0 6	67. 58	16. 22	82.31
Pt-0.005	320	1	80.0 9	16.2 8	58. 07	18. 15	61.04
	320	2	70.1 7	4.24	46. 24	49. 51	67.18
Pt-0.003	320	1	72.1 6	8.91	58. 41	22. 85	58.66
	320	2	42.1 9	8.18	53. 2	38. 62	38.74

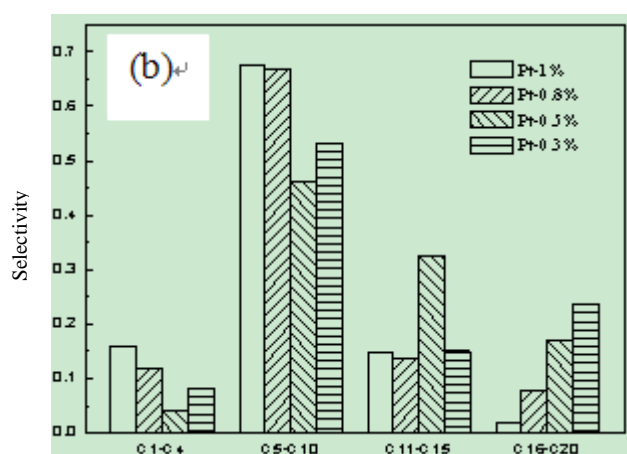
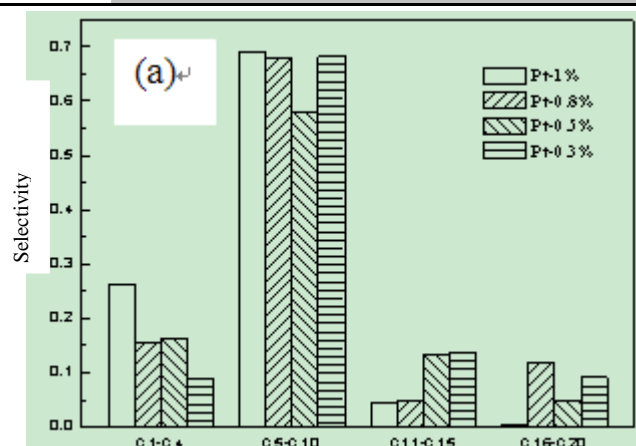


FIG. 2 SELECTIVITY OF Pt/SAB CATALYST WITH DIFFERENT WHSV= 1 h^{-1} (a) AND WHSV= 2 h^{-1} (b)

The previous study showed that NiW/SAB catalyst

had 92.18% conversion ratio and 84.39% naphtha and MD yield with the conditions of $T = 320\text{ }^{\circ}\text{C}$, $P = 3.5\text{ MPa}$, $\text{WHSV} = 1\text{ h}^{-1}$, and $\text{H}_2/\text{wax} = 0.12\text{ wt/wt}$. Pt-0.008 catalyst shows similar naphtha and MD yield, but higher conversion ratio and higher WHSV, and that Pt-0.008 catalyst has better catalytic properties compared to NiW/SAB catalyst.

Fig 3. shows the selectivity of final product distribution with different Pt loading. The products are defined as four groups as $\text{C}_1\text{-C}_4$, $\text{C}_5\text{-C}_{10}$, $\text{C}_{11}\text{-C}_{15}$ and $\text{C}_{16}\text{-C}_{20}$. With the WHSV increasing from 1 h^{-1} to 2 h^{-1} , the selectivity of $\text{C}_1\text{-C}_4$ decreases gradually and $\text{C}_5\text{-C}_{10}$ keeps the same. The selectivity of $\text{C}_{11}\text{-C}_{15}$ increases significantly. Thereof, Pt-0.01 and Pt-0.008 catalysts show higher selectivity of $\text{C}_5\text{-C}_{10}$ and $\text{C}_{11}\text{-C}_{15}$.

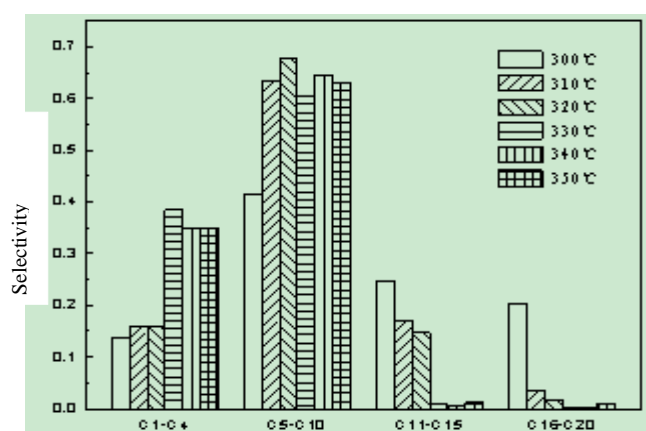


FIG. 3 SELECTIVITY OF Pt/SAB CATALYST WITH DIFFERENT TEMPERATURE

Catalytic Activity of Pt/SAB Catalyst with Different Temperature

TABLE 3 EFFECT OF DIFFERENT TEMPERATURE ON PT/SAB CATALYST ACTIVITY

Selectivity(%)						
T (°C)	WH SV (h ⁻¹)	Conve rsion (%)	Gas	Naph.	MD	Naph. and MD yield(%)
300	2	90.74	13.60	41.50	44.93	78.43
310	2	96.50	16.04	63.41	20.55	81.02
320	2	98.22	16.06	67.58	16.22	82.31
330	2	99.54	38.48	60.45	1.11	61.28
340	2	94.74	34.76	64.43	0.82	61.82
350	2	90.41	34.69	62.94	2.1	58.8

Pt-0.008/SAB catalyst was selected to present the catalyst performance and the temperature was set from $300\text{ }^{\circ}\text{C}$ to $350\text{ }^{\circ}\text{C}$. Since Pt had high activity, the WHSV was adjusted to 2 h^{-1} and it could help increase the selectivity of middle distillates while keeping suitable conversion rate. The conversion ratio and selectivity are shown in Table 3. The results showed that the conversion ratio and selectivity of naphtha

and MD are similar when the temperature changes from $310\text{ }^{\circ}\text{C}$ to $320\text{ }^{\circ}\text{C}$. The selectivity of naphtha and MD decreases when the temperature increases from $330\text{ }^{\circ}\text{C}$ to $350\text{ }^{\circ}\text{C}$.

The relationship between different temperature and product distribution is shown in Fig 4. With the temperature increasing from $300\text{ }^{\circ}\text{C}$ to $330\text{ }^{\circ}\text{C}$, the conversion ratio is improved. The conversion ratio decreases when temperature is higher than $340\text{ }^{\circ}\text{C}$. The results indicate that more gas components ($\text{C}_1\text{-C}_4$) are generated at higher temperature, which shows that Pt-0.008/SAB catalyst has higher activity and over hydrocracking reaction generated. The selectivity of $\text{C}_5\text{-C}_9$ and $\text{C}_{10}\text{-C}_{18}$ fractions reaches peak at $320\text{ }^{\circ}\text{C}$ and decreases significantly with the increasing temperature. In general, the conversion ratio of Pt-0.008/SAB catalyst is higher than NiW/SAB catalyst and the selectivity is mostly the same. This identifies that Pt/SAB catalyst with larger surface area and pore size enhances the activity of the catalyst.

Catalytic Activity of Pd/SAB Catalyst with Different Temperature and WHSV

In order to understand further the activity of Pd/SAB catalyst, another study was carried out on the selected Pd-0.008/SAB catalyst. The catalytic performance of the Pd-0.008/SAB catalyst was measured at $T=260\text{-}300\text{ }^{\circ}\text{C}$, $P=3.5\text{ MPa}$, $\text{H}_2/\text{wax} = 0.12\text{ wt/wt}$ and $\text{WHSV}=1\text{-}3\text{ h}^{-1}$.

TABLE 4 EFFECT OF DIFFERENT TEMPERATURE AND WHSV ON PD/SAB CATALYST ACTIVITY

Selectivity(%)						
T (°C)	WH SV (h ⁻¹)	Conversi on (%)	Gas	Naph.	MD	Naph. and MD yield(%)
260	1	41.29	12.11	52.94	34.95	38.30
280	1	96.26	60.35	37.76	2.12	38.39
300	1	98.53	59.69	39.94	0.38	39.73
300	2	78.59	46.62	39.74	13.56	41.89
300	3	66.09	38.49	35.64	26.01	40.74

The catalytic activities of Pd/SAB catalyst with different temperature and WHSV are presented in Table 4. The catalyst shows the lower conversion ratio when temperature is $260\text{ }^{\circ}\text{C}$. The conversion ratio is increased significantly when the temperature reaches 280 and $300\text{ }^{\circ}\text{C}$. The naphtha and MD yield are almost the same with different temperature. The conversion ratio decreases with higher WHSV. Fig. 4 shows that Pd/SAB catalyst has high gas products selectivity since the strongly acidic catalysts promote the deeper

hydrocracking reaction.

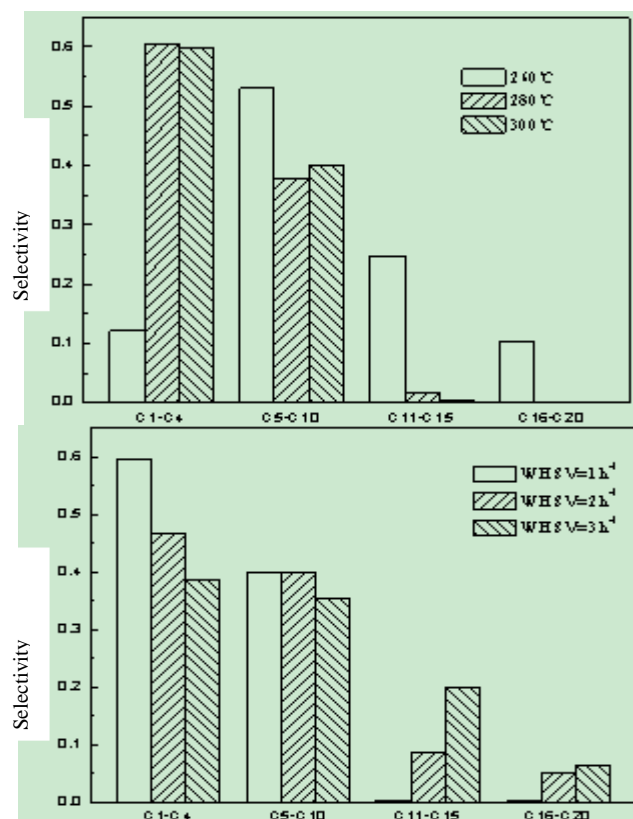


FIG. 4 SELECTIVITY OF Pd/SAB CATALYST WITH DIFFERENT TEMPERATURE AND WHSV

Deactivation Properties of NiW/SAB and Pt/SAB Catalyst

Deactivation behaviors of NiW/SAB, Pd/SAB and Pt/SAB catalysts were investigated under the same hydrocracking reactions. In this study, Pt-0.008/SAB and Pd-0.008/SAB catalysts were selected as standard to test the deactivation properties. The results (Fig.4) showed that Pd-0.008/SAB catalyst was deactivated after 38 h and fresh NiW/SAB catalyst was deactivated after 130 h, whereas Pt/SAB catalyst showed good catalytic activity after 200 h. Increasing temperature can't help increase the conversion ratio of NiW/SAB and Pd/SAB catalyst. The deactivated NiW/SAB catalyst was re-sulfured and deactivated again after 30 h. Loss of sulfur is the main reason for NiW/SAB catalyst deactivation. The TEM (Fig 5) shows that Pt/SAB catalyst is stable after 200 h reaction since the metal is not changed significantly. It is clear that Pt is dispersed well and stable in comparison with Pd that is lost after reaction as shown in Fig 5. ICP results show that the Pd amount of reacted Pd/SAB catalyst is only 20% of fresh catalyst. While the Pt amount of reacted Pt/SAB catalyst reaches 85% fresh catalyst. It is confirmed that Pd is lost, but Pt is more stable and reactive.

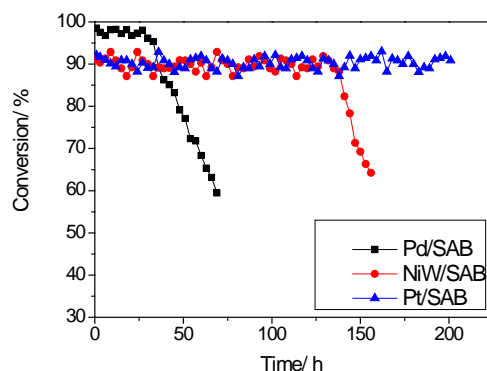


FIG. 5 DEACTIVATION PROPERTIES OF DIFFERENT CATALYSTS

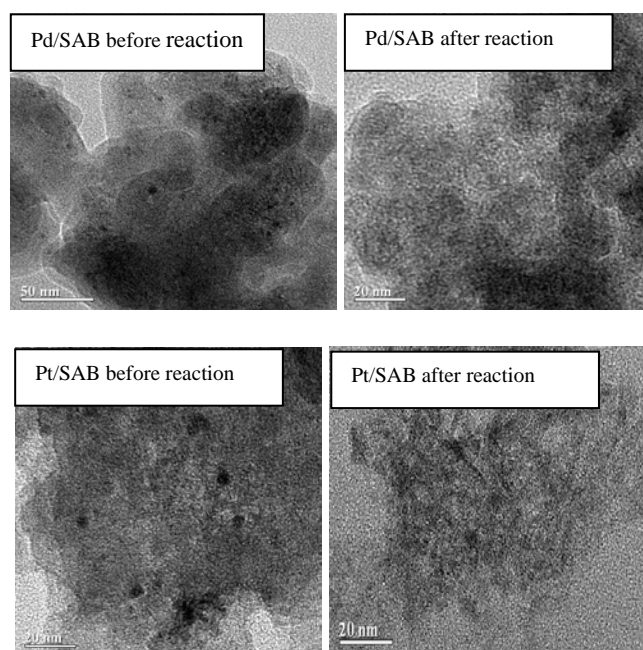


FIG.6 TEM IMAGE OF Pd/SAB AND Pt/SAB CATALYST (BEFORE AND AFTER REACTION)

Textural properties including surface area and average pore diameter of different catalysts are summarized in Table 5. All catalysts have decreases of textural properties after reaction. Therefore, the surface area of Pd/SAB catalyst decreases significantly while NiW/SAB and Pt/SAB catalyst decreases slightly.

TABLE 5 SURFACE PROPERTIES OF FRESH AND USED CATALYSTS

Catalysts	S _{BET} (m ² /g)		APD (nm)	
	Fresh	Used	Fresh	Used
NiW/SAB	188	177	9.9	9.1
Pt-0.008/SAB	240	228	9.8	9.6
Pd-0.008/SAB	223	189	9.9	8.4

Conclusion

The different temperature and Pt loading have been investigated via fixed bed reactor 0.8 wt% Pt loading catalyst had similar selectivity of C₅-C₁₅ and higher

conversion ratio compared with NiW/SAB catalyst while WHSV was increased from 1 h⁻¹ to 2 h⁻¹ and temperature was 20°C lower. It was observed that the conversion rate of Pt/SAB catalyst increased with larger surface area and pore volume. Pd-0.008/SAB catalyst had higher activity, which led to higher gas selectivity and lower naphtha and MD selectivity.

The deactivation behaviors showed that NiW/SAB catalyst loses activity after 137 h while Pt/SAB catalyst kept the activity for more than 200 h. TEM showed that Pt was dispersed well and stable in catalyst. The re-sulfuric NiW/SAB catalyst lost the activity after 30 h, which indicated that the deactivation was caused by loss of sulfur. Pd/SAB catalyst lost activity after 38 h which has been identified by losing of metal.

It was concluded that Pt/SAB had more stable deactivation properties, while conversion ratio was higher and middle distillate selectivity was similar to NiW/SAB catalyst with more mild conditions, such as higher WHSV and lower temperature.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from National Natural Science Fund (contract number is 21076082) and the sub subject of the National 863 plan (contract number is 2011AA05A2031).

REFERENCES

- Arroyo, J.A. Muñoz, Martens, G.G., Froment, G.F., Marin, G.B., Jacobs, P.A., Martens, J.A., APPL. CATAL. A-GEN 192 (2000) 9-22.
- Bouchy, C., Hastoy, G., Guillon, E., Martens, J.A., OIL GAS SCI. TECHNOL.-Rev. IFP, 64 (2009) 91-112.
- Calemma, V., Gambaro, C., W.O.P. Jr., Carbone, R., Giardino, R., Scorletti, P., CATAL. TODAY. 149 (2010) 40-46.
- Cho, K.M., Park, S., Seo, J.G., Youn, M.H., Nam, I., Baeck, S.H., Chung, J.S., Jun, K.W., Song, I.K., CHEM. ENG. J. 146 (2009) 307-314.
- Christian, M., Catalyse acido-basique, application au raffinage et à la pétrochimie. Publications de l'institut français du pétrole: Pairs. 2003, pp.821
- Clark, J.R., Wittenbrink, R.J., Ryan, D.F., Schweizer, A.E., US6375830, 2002
- Collins, J.P., Freide, J.J.H.M.F., Nay, B., J. NAT. GAS. CHEM. 15 (2006) 1-10.
- Hwang, S., Lee, J., Seo, J.G., Park, D.R., Youn, M.H., Jung, J.C., Lee, S.B., Song, I.K., CATAL. LETT. 132 (2009) 410-416.
- Jiang, J., Dong, Z.H., Chen, H.Y., Sun, J.B., Yang, C., Cao, F.H., ENERG FUEL. 27(2013) 1035-1039.
- Leckel, D., ENERG FUEL, 21 (2007) 1425-1431.
- Leckel, D., Liwanga-Ehumbu, M., ENERG FUEL, 20 (2006) 2330-2336.
- Lee, J., Hwang, S., Park, D.R., Seo, J.G., Youn, M.H., Jung, J.C., Lee, S.B., Chung, J.S., Song, I. K., Korean J. Chem. Eng. 27 (2010) 807-811.
- Lee, J., Hwang, S., Seo, J.G., Hong, U.G., Jung, J.C., Song, I.K., J. IND. ENG. CHEM. 17 (2011) 310-315.
- Leyva, C., Rana, M.S., Trejo, F., Ancheyta, J., IND. ENG. CHEM. RES. 46 (2007) 7448-7466.
- Liu, Y., Murata, K., Okabe, K., Inaba, M., Takahara, I., Hanaoka, T., Sakanishi, K., TOP CATAL. 52 (2009) 597-608.
- Möller, K., le Grange, P., Accolla, C., IND. ENG. CHEM. RES, 48 (2009) 3791-3801.
- Nam, I., Cho, K.M., Seo, J.G., Hwang, S., Jun, K.W., Song, I.K., CATAL. LETT. 130 (2009) 192-197.
- Puskas, I., Hurlbut, R.S., CATAL. TODAY. 84 (2003) 99-109.
- Sanchez, J., Tallafigo, M.F., Gilarranz, M.A., Rodriguez, F., Ind. Eng. Chem. Res. 47 (2008) 6854-6861.
- Seki, H., Aoki, N., Ikeda, M., Upgrading of Heavy Oils and Resids, 30 Years Progress Since the First Oil Crisis, American Chemical Society, Washington, DC, 2003, pp. 139-140
- Toulhoat, H., Raybaud, P., Benazzi, E., J. CATAL. 221 (2004) 500-509.
- Vliet, O.P.R. Van, Faaij, A.P.C., Turkenburg, W.C., ENERG. CONVERS. MANAGE. 50 (2009) 855-876.